

**High-Accuracy Quartic Force Field Calculations for the  
Spectroscopic Constants and Vibrational Frequencies of  $1^1A'$   
 $l$ -C<sub>3</sub>H<sup>-</sup>: A Possible Link to Lines Observed in the Horsehead  
Nebula PDR**

Ryan C. Fortenberry

NASA Ames Research Center, Moffett Field, CA 94035-1000, U.S.A.

Xinchuan Huang

SETI Institute, 189 Bernardo Avenue, Suite 100, Mountain View, CA 94043, U.S.A.

T. Daniel Crawford

Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, U.S.A.

Timothy J. Lee

`Timothy.J.Lee@nasa.gov`

NASA Ames Research Center, Moffett Field, CA 94035-1000, U.S.A.

April 23, 2013

Received \_\_\_\_\_; accepted \_\_\_\_\_

## ABSTRACT

It has been shown that rotational lines observed in the Horsehead nebula PDR are probably not caused by  $l\text{-C}_3\text{H}^+$ , as was originally suggested. In the search for viable alternative candidate carriers, quartic force fields are employed here to provide highly accurate rotational constants, as well as fundamental vibrational frequencies, for another candidate carrier:  $1\ ^1A'\ \text{C}_3\text{H}^-$ . The *ab initio* computed spectroscopic constants provided in this work are, compared to those necessary to define the observed lines, as accurate as the computed spectroscopic constants for many of the known interstellar anions. Additionally, the computed  $D_{eff}$  for  $\text{C}_3\text{H}^-$  is three times closer to the  $D$  deduced from the observed Horsehead nebula lines relative to  $l\text{-C}_3\text{H}^+$ . As a result,  $1\ ^1A'\ \text{C}_3\text{H}^-$  is a more viable candidate for these observed rotational transitions and would be the seventh confirmed interstellar anion detected within the past decade and the first  $\text{C}_n\text{H}^-$  molecular anion with an odd  $n$ .

**Keywords:** astrochemistry – ISM: individual objects: Horsehead nebula – ISM: lines and bands – ISM: molecules – molecular data – radio lines: ISM

## 1. Introduction

Recent work by Huang et al. (2013) has questioned the attribution of lines observed in the Horsehead nebula photon-dominated-region (PDR) to  $l\text{-C}_3\text{H}^+$ . Quartic force fields (QFFs) computed from high-level *ab initio* quantum mechanical energies analyzed using perturbation theory at second order (Papousek & Aliev 1982) are known to produce highly accurate spectroscopic constants. Even though the  $B_0$  computed by Huang et al. (2013) (11 262.68 MHz) is within 0.16% of the  $B$ -type rotational constant derived from the

observations by Pety et al. (2012) (11 244.9474 MHz), the computed  $D_e$  of 4.248 kHz differs by 44.5% from the observed  $D$  value of 7.652 kHz. This “error” is more than an order of magnitude larger than any other error for a computed  $D_e$  of a cation (using similar levels of theory) as compared to known high-resolution experimental data. Furthermore, the sextic distortion constant,  $H$ , differs by three orders of magnitude. As a result, it is unlikely that  $l\text{-C}_3\text{H}^+$  corresponds to the lines observed by Pety et al. (2012).

This result motivates the question, “What is the carrier of these lines?” If these observed lines are, in fact, related to one another, certain inferences can be made about the molecular carrier. To match the rotational constants derived from the transition energies corresponding to the observed lines, the carrier is either linear or quasi-linear, almost certainly composed of three carbon atoms as well as a single hydrogen atom, and closed-shell since there are no splittings in the lines as required for the rotational spectra of open-shell molecules (McCarthy 2013). All of these criteria are, in fact, met by  $l\text{-C}_3\text{H}^+$ , but this cation’s difference between observational and high-accuracy theoretical rotational constants, especially the  $D$  constant, discussed above and by Huang et al. (2013), probably rules it out. As a result, the quasi-linear anion,  $1\ ^1A'\ l\text{-C}_3\text{H}^-$ , remains as the most likely candidate carrier of the Horsehead nebula PDR rotational lines of interest.

Even though the most stable singlet isomer of  $\text{C}_3\text{H}^-$  is the cyclic form,  $c\text{-C}_3\text{H}^-$ , the barrier to isomerization is high enough (45 kcal mol $^{-1}$ ) for the quasi-linear  $C_s$  isomer to be kinetically stable (Lakin et al. 2001). Various mechanisms for interstellar synthesis of this anion are possible (Larsson et al. 2012; Senent & Hochlaf 2013) and are probably related to those responsible for the creation of the related  $\text{C}_{2n}\text{H}^-$  for  $n = 2 - 4$  anions previously detected in the interstellar medium (ISM) (McCarthy et al. 2006; Cernicharo et al. 2007; Brünken et al. 2007b). Furthermore, radical  $\text{C}_3\text{H}$  in both the linear and cyclic forms has also been detected in the ISM (Thaddeus et al. 1985; Yamamoto et al. 1987) suggesting the

possible interstellar existence of the anion.

Additionally,  $\text{C}_3\text{H}^-$  is of astronomical interest since it has been computationally shown by Fortenberry (2013) to possess not only a rare dipole-bound singlet excited electronic state (the  $2\ ^1A'$  state) but also an even more rare valence excited state ( $1\ ^1A''$ ) below the electron binding or electron detachment energy. In fact, the valence electronically excited state is the only such state thus far proposed to exist for an anion of this size which also contains only first-row atoms (Fortenberry & Crawford 2011b,a; Fortenberry 2013). Furthermore, anions have been proposed as carriers of some diffuse interstellar bands (DIBs) (Sarre 2000; Cordiner & Sarre 2007; Fortenberry et al. 2013a), and  $\text{C}_3\text{H}^-$  has unusual properties that may be of importance to the DIBs.

## 2. Computational Details

The spectroscopic constants and fundamental vibrational frequencies of  $1\ ^1A'$   $l\text{-C}_3\text{H}^-$  are computed through the established means of QFFs (Huang & Lee 2008). Starting from a restricted Hartree-Fock (RHF) (Scheiner et al. 1987) coupled cluster (Lee & Scuseria 1995; Shavitt & Bartlett 2009; Crawford & Schaefer 2000) singles, doubles, and perturbative triples [CCSD(T)] (Raghavachari et al. 1989) aug-cc-pV5Z (Dunning 1989; Kendall et al. 1992; Dunning et al. 2001) geometry further corrected for core correlation effects from the Martin-Taylor (MT) basis set (Martin & Taylor 1994), a grid of 743 symmetry-unique points is generated. Simple-internal coordinates for the bond lengths and  $\angle \text{H-C-C}$  are coupled to linear LINX and LINY (Allen & coworkers 2005) coordinates exactly as those defined in Fortenberry et al. (2012b) for  $\text{HOCO}^+$ . Displacements of 0.005 Å for the bond lengths, 0.005 rad for the bond angle, and 0.005 for the LINX and LINY coordinates and

the associated energies computed at each point define the QFF, which is of the form:

$$V = \frac{1}{2} \sum_{ij} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{ijk} F_{ijk} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{ijkl} F_{ijkl} \Delta_i \Delta_j \Delta_k \Delta_l, \quad (1)$$

where  $\Delta_i$  are the displacements and  $F_{ij\dots}$  are force constants (Huang & Lee 2008).

At each point, CCSD(T)/aug-cc-pVXZ (where  $X = T, Q, 5$ ) energies are computed and extrapolated to the complete basis set (CBS) limit via a three-point formula (Martin & Lee 1996). Additionally, energy corrections are made to the CBS energy for core correlation and for scalar relativistic effects (Douglas & Kroll 1974). The resulting QFF is denoted as the CcCR QFF for the CBS energy, core correlation correction, and scalar relativistic correction, respectively, (Fortenberry et al. 2011). The augmented Dunning basis sets have been shown by Skurski et al. (2000) to be reliable for computations of anionic properties. An initial least-squares-fit of the CcCR energy points leads to a minor transformation of the reference geometry such that the gradients are identically zero. This geometry and the resulting force constants are then employed in the rovibrational computations. All electronic structure computations make use of the MOLPRO 2010.1 quantum chemical package (Werner et al. 2010), and all employ the Born-Oppenheimer approximation making the QFFs identical for the isotopologues.

The QFF is fit from the 805 redundant total energy points with a sum of squared residuals on the order of  $3 \times 10^{-17}$  a.u.<sup>2</sup> Cartesian derivatives are then computed from the QFF with the INTDER program (Allen & coworkers 2005). From these, the SPECTRO program (Gaw et al. 1991) employs second-order vibrational perturbation theory (VPT2) to generate the spectroscopic constants (Papousek & Aliev 1982) and vibrational frequencies (Mills 1972; Watson 1977). After transforming the force constants into the Morse-cosine coordinate system so that the potential possesses proper limiting behavior (Dateo et al. 1994; Fortenberry et al. 2013b), vibrational configuration interaction (VCI) computations with the MULTIMODE program (Carter et al. 1998; Bowman et al. 2003) also produce

vibrational frequencies. The VCI computations make use of the same basis set and wavefunction construction as that utilized by Fortenberry et al. (2012b,a) in similar quasi-linear tetra-atomic systems.

### 3. Discussion

The force constants computed in this study are listed in Table 1. The CcCR geometrical parameters and spectroscopic constants are given in Table 2 for both  $1^1A'$   $l$ -C<sub>3</sub>H<sup>-</sup> and the deuterated isotopologue. The equilibrium dipole moment is computed with respect to the center-of-mass with CCSD(T)/aug-cc-pV5Z to be 2.16 D. The C–C–C  $R_\alpha$  vibrationally-averaged bond angle is nearly collinear at 174.540° while the H–C–C vibrationally-averaged bond angle is 109.491°. These values are in line with those computed by Lakin et al. (2001). As has been discussed by Fortenberry (2013) for C<sub>3</sub>H<sup>-</sup>, the C<sub>1</sub> carbon atom adjacent to the hydrogen atom shown in Figure 1 is a carbene-type carbon containing a lone pair which leads to a longer C<sub>1</sub>–C<sub>2</sub> bond length compared to the shorter C<sub>2</sub>–C<sub>3</sub> bond length. Even though this result differs from the CCSD(T) results from Lakin et al. (2001), their reported CASSCF and HF results give bond lengths similar to ours leading us to conclude that the CCSD(T) C–C bond lengths are mislabeled in the paper by Lakin et al. (2001). The vibrationally-averaged geometrical parameters change slightly upon deuteration. Similar bond angles of the heavy atoms have been computed for the *trans*-HOCO<sup>+</sup>, HOCS<sup>+</sup>, and HSCO<sup>+</sup> systems (Fortenberry et al. 2012b,a) with very good agreement present for known experimental data.

The most notable values in Table 2 are the rotational constants and the quartic centrifugal distortion ( $D$ -type) constants. For  $1^1A'$   $l$ -C<sub>3</sub>H<sup>-</sup>, the  $B_0$  rotational constant is 11 339.66 MHz while  $C_0$  is 11 087.35 MHz. The equilibrium constants are slightly larger, but both sets are in reasonable agreement with those computed by Lakin et al. (2001). The

$D$ -type constants have not been vibrationally averaged, and  $D_J$ , most prominently, is 4.954 kHz.

Direct comparison between these values and those deduced from the Horsehead nebula PDR spectrum observed by Pety et al. (2012) is not possible since the isomer of  $C_3H^-$  of interest here is not perfectly linear. Pety et al. (2012) assume a linear structure in order to fit the effective rotational constant,  $B_{eff}$ , and the effective centrifugal distortion constant,  $D_{eff}$  and use the second-order fitting equation,

$$\nu_{J+1 \rightarrow J} = 2B(J+1) - 4D(J+1)^3, \quad (2)$$

to compute the affiliated rotational constants.  $C_3H^-$  is non-linear and requires the following related equation from McCarthy et al. (1997):

$$\nu_{J+1 \rightarrow J} = (B+C)(J+1) - \left\{ 4D_J + \frac{(B-C)^2}{c \left[ A - \frac{(B+C)}{2} \right]} \right\} (J+1)^3, \quad (3)$$

with the assumption that  $K = 0$  forcing  $c = 8$ . As such, we can set Equation 2 equal to Equation 3. The  $(J+1)$  term in Equation 3 is equal to  $2B_{eff}$ , and the  $(J+1)^3$  term in Equation 3 is equal to  $4D_{eff}$ . Using the CcCR computed  $A_0$ ,  $B_0$ ,  $C_0$ , and  $D_J$  values, where  $D_J$  is the only equilibrium constant,  $B_{eff}$  is computed to be 11 213.51 MHz, and  $D_{eff}$  is 8.795 kHz. Hence, direct comparison between the CcCR  $C_3H^-$  rotational constants and those obtained from the lines observed by Pety et al. (2012) is possible.

The second-order fit of the lines observed by Pety et al. (2012) indicates that the carrier must have a  $B/B_{eff}$  that is very close to 11 244.9474 MHz and a  $D/D_{eff}$  that is 7.652 kHz. The  $B_{eff}$  computed with the  $A_0$ ,  $B_0$ , and  $C_0$  rotational constants by the above approach is very close, off by 31.44 MHz or 0.28%. This is roughly the same difference between the observed  $B$  and that of  $l$ - $C_3H^+$  (Huang et al. 2013) and is typical of the accuracies that can be expected when comparing QFF computations with the CCSD(T) level of theory to experiment as enumerated in Table 3. However, the 8.795 kHz  $D_{eff}$  for  $1^1A'$   $l$ - $C_3H^-$  is

much closer to the 7.652 kHz  $D$  derived from the lines observed by Pety et al. (2012) in the Horsehead nebula than the linear cation (Huang et al. 2013). Even so, this  $D_{eff}$  of 8.795 kHz differs from the observation by 1.14 kHz or 14.93%. Replacing  $A_0$ ,  $B_0$ , and  $C_0$  with  $A_e$ ,  $B_e$ , and  $C_e$  in Equation 3 lowers the  $C_3H^-$   $D_{eff}$  to 8.366 kHz, a difference of 0.714 kHz or 9.34% from that determined by Pety et al. (2012).

Table 3 provides some insight into the accuracies that can be expected for calculated rotational constants of similar molecules. The quasi-linear cations listed below  $C_3H^-$  show strong correlation between the computed  $B_{eff}$  from the use of  $B_0$  and  $C_0$  and the  $B_{eff}$  derived from the various experiments. Additionally, the  $D_{eff}$  values computed the same way with the equilibrium  $D_J$  also show good, albeit not as strong, correlation between theory and experiment. Unfortunately,  $C_3H^-$  has errors that are larger than this. However, this probably results from a combination of basis set incompleteness and higher-order correlation effects. Even though aug-cc-pVXZ basis sets used at the CCSD(T) level of theory have been shown to be effective in the computation of anionic properties (Skurski et al. 2000; Fortenberry & Crawford 2011b), higher-order properties such as the  $D$ -type constants are more susceptible to even the smallest errors. This is clear in the cations, as well, where the  $D_{eff}$  values are not as accurate as the  $B_{eff}$  values.

The known interstellar anions and the related  $C_2H^-$  system, which has not yet been detected in the ISM, are linear and have  $B$  and  $D$  computed directly, most often as  $B_e$  and  $D_e$ . Note that the theoretical rotational constants are not as accurate for the anions as they are for the cations. Most notably, the  $B_e/B_0$  and  $D_e$  values computed with a CCSD(T)/aug-cc-pCV5Z cubic force field for  $C_5N^-$  by Botschwina & Oswald (2008) are directly used in the identification of this anion in the ISM (Cernicharo et al. 2008). As listed in Table 3, agreement between computed  $B$  values and that necessary to match the observed rotational lines actually worsens when  $B_0$  is used instead of  $B_e$ , more than



doubling the percent error. This is the same behavior as what is currently found for  $\text{C}_3\text{H}^-$ . Additionally, the  $D_e$  percent error for  $\text{C}_5\text{N}^-$ , as compared to observation, is 9.1%, almost exactly what it is for  $\text{C}_3\text{H}^-$  when using the equilibrium rotational constants. The force field employed by Botschwina & Oswald (2008) also includes core correlation like the CcCR QFF. Hence, the present rotational constants are in the same accuracy range for  $\text{C}_3\text{H}^-$  as those used to detect  $\text{C}_5\text{N}^-$  in the ISM.

Furthermore, Senent & Hochlaf (2010) compute  $B_e$  for  $\text{C}_4\text{H}^-$  to be in error compared to experiment by nearly twice as much as  $B_{eff}$  for  $\text{C}_3\text{H}^-$  utilizing  $A_0$ ,  $B_0$ , and  $C_0$  in the formulation here. The  $\text{C}_2\text{H}^-$   $B_e$  is in error compared to experiment by roughly an equivalent amount as  $B_{eff}$  for  $\text{C}_3\text{H}^-$ . Also,  $D_e$  for  $\text{C}_6\text{H}^-$  and  $\text{C}_8\text{H}^-$  is in the same error range as the present  $\text{C}_3\text{H}^-$   $D_{eff}$ .  $\text{C}_3\text{N}^-$  behaves similarly. The CCSD(T)/aug-cc-pCV5Z  $B_e$  and  $D_e$  for  $\text{CN}^-$  are much more accurate than any other system shown here, but it has fewer electrons and fewer degrees of freedom than any other. Regardless, our accuracies in the computation of  $B_{eff}$  and  $D_{eff}$  for  $1^1A'$   $\text{C}_3\text{H}^-$  are comparable to those obtained for other interstellar anions. Hence,  $\text{C}_3\text{H}^-$  is, perhaps, the most viable candidate for the carrier of the rotational lines observed in the Horsehead nebula previously attributed to  $l\text{-C}_3\text{H}^+$  (Pety et al. 2012).

Comparison of the sextic distortion constant,  $H_{eff}$ , is not as straightforward. There is a dearth of data on how the computation of this value for anions compares to experiment.  $H_J$ , which is an equilibrium value, is not exactly  $H_{eff}$ , but they are probably related. Even though  $H$  obtained by Pety et al. (2012) is 560 mHz and  $H_J$  for  $\text{C}_3\text{H}^-$  is 3.344 mHz, this is an order of magnitude closer agreement than this same  $H$  compared to the  $H_e$  for  $l\text{-C}_3\text{H}^+$ , 0.375 mHz (Huang et al. 2013). Additionally, the same basis set and correlation errors for anions that affect the calculation of  $D$  will be present for  $H$ . As a result, we can only say here that as far as  $H$  is concerned for comparison to the lines observed in the Horsehead nebula by Pety et al. (2012),  $1^1A'$   $\text{C}_3\text{H}^-$  is a better candidate than  $l\text{-C}_3\text{H}^+$ .

The harmonic and anharmonic vibrational frequencies for both  $1^1A'$   $l$ -C<sub>3</sub>H<sup>-</sup> and  $l$ -C<sub>3</sub>D<sup>-</sup> are given in Table 4. Positive anharmonicities are present in both isotopologues for the  $\nu_5$  C<sub>1</sub>–C<sub>2</sub>–C<sub>3</sub> bending and the  $\nu_6$  torsional modes. VPT2 and VCI produce fundamental vibrational frequencies from the CcCR QFF that are quite consistent. The largest deviation between the methods, 1.0 cm<sup>-1</sup>, is found for the  $\nu_4$  H–C<sub>1</sub>–C<sub>2</sub> bending mode. Comparison of the C<sub>3</sub>H<sup>-</sup> CcCR QFF vibrational frequencies, whether computed using VPT2 or VCI, to those computed by Lakin et al. (2001) is roughly consistent for  $\nu_1$ – $\nu_4$ . The  $\nu_5$  anharmonic frequencies differ by more than 50 cm<sup>-1</sup>, though the  $\omega_5$  harmonic frequencies are very similar (i.e., the difference in the  $\nu_5$  fundamental frequency is mostly due to differences in the anharmonic correction). The torsional mode is nearly identical between the two studies, though in this case the harmonic frequencies differ by more than 50 cm<sup>-1</sup>. It is hoped that the present QFF computations of the fundamental vibrational frequencies provided here will assist in the characterization of this anion in current and future studies of the ISM or simulated laboratory experiments at infrared wavelengths in addition to studies in the sub-millimeter spectral region.

#### 4. Conclusions

Since the link between  $l$ -C<sub>3</sub>H<sup>+</sup> and the lines observed in the Horsehead nebula PDR by Pety et al. (2012) has recently been strongly questioned by Huang et al. (2013), another viable candidate is necessary. The rotational lines seem to require a closed-shell quasi-linear structure composed of three carbon atoms along with a hydrogen atom.  $1^1A'$  C<sub>3</sub>H<sup>-</sup> appears to be the most likely candidate. Here, the CcCR QFF has determined a  $B_{eff}$  for this anion to be in error by 0.28% from that required to fit the observed lines. The use of the equilibrium rotational constants fortuitously lowers the error to 0.11%. However, the error reduction and error magnitudes themselves are in line with the computed C<sub>5</sub>N<sup>-</sup> rotational

constants used in its interstellar detection. Additionally, the discrepancy between the  $A_e$ ,  $B_e$ , and  $C_e$  computed  $C_3H^-$   $D_{eff}$  and the  $D_{eff}$  deduced from the observed interstellar rotational lines is similar to the  $D_e$  errors for  $C_4H^-$ ,  $C_3N^-$ , and  $C_5N^-$  and less than that of  $C_6H^-$ , which are all reported for CCSD(T) computations, *i.e.* similar levels of theory. Hence, the consistency of the errors for  $C_3H^-$  with other anions previously detected in the ISM coupled with its matching the required spectral criteria make this anion the strongest candidate carrier for the Horsehead nebula PDR lines and, potentially, the most recent anion detected in the ISM. It would also be the first detected interstellar odd-numbered monohydrogen carbon chain anion.

## 5. Acknowledgements

RCF is currently supported on a NASA Postdoctoral Program Fellowship administered by Oak Ridge Associated Universities. NASA/SETI Institute Cooperative Agreement NNX12AG96A has funded the work undertaken by XH. Support from NASA’s Laboratory Astrophysics ‘Carbon in the Galaxy’ Consortium Grant (NNH10ZDA001N) is gratefully acknowledged. The U.S. National Science Foundation (NSF) Multi-User Chemistry Research Instrumentation and Facility (CRIF:MU) award CHE-0741927 provided the computational hardware, and award NSF-1058420 has supported TDC. The CheMVP program was used to create Fig. 1.

## REFERENCES

- Allen, W. D., & coworkers. 2005, *INTDER* 2005 is a general program written by W. D. Allen and coworkers, which performs vibrational analysis and higher-order non-linear transformations.
- Bogey, M., Demuyne, C., Destombes, J. L., & Krupnov, A. 1988, *JMoSt*, 190, 465
- Botschwina, P., & Oswald, R. 2008, *JChPh*, 129, 044305
- Bowman, J. M., Carter, S., & Huang, X. 2003, *Int. Rev. Phys. Chem.*, 22, 533
- Brünken, S., Gottlieb, C. A., Gupta, H., McCarthy, M. C., & Thaddeus, P. 2007a, *A&A*, 464, L33
- Brünken, S., Gupta, H., Gottlieb, C. A., McCarthy, M. C., & Thaddeus, P. 2007b, *ApJL*, 664, 43
- Carter, S., Bowman, J. M., & Handy, N. C. 1998, *Theor. Chem. Acc.*, 100, 191
- Cernicharo, J., Guélin, M., Agúndez, M., et al. 2007, *A&A*, 467, L37
- Cernicharo, J., Guélin, M., Agúndez, M., McCarthy, M. C., & Thaddeus, P. 2008, *ApJ*, 688, L83
- Cordiner, M. A., & Sarre, P. J. 2007, *A&A*, 472, 537
- Crawford, T. D., & Schaefer, H. F. 2000, in *Reviews in Computational Chemistry*, ed. K. B. Lipkowitz & D. B. Boyd, Vol. 14 (New York: Wiley), 33–136
- Dateo, C. E., Lee, T. J., & Schwenke, D. W. 1994, *JChPh*, 101, 5853
- Douglas, M., & Kroll, N. 1974, *AnPhy*, 82, 89
- Dunning, T. H. 1989, *JChPh*, 90, 1007

- Dunning, T. H., Peterson, K. A., & Wilson, A. K. 2001, JChPh, 114, 9244
- Fortenberry, R. C. 2013, Mol. Phys., *in press*
- Fortenberry, R. C., & Crawford, T. D. 2011a, JPCA, 115, 8119
- . 2011b, JChPh, 134, 154304
- Fortenberry, R. C., Crawford, T. D., & Lee, T. J. 2013a, ApJ, 762, 121
- Fortenberry, R. C., Huang, X., Francisco, J. S., Crawford, T. D., & Lee, T. J. 2011, JChPh, 135, 134301
- . 2012a, JPCA, 116, 9582
- . 2012b, JChPh, 136, 234309
- Fortenberry, R. C., Huang, X., Yachmenev, A., Thiel, W., & Lee, T. J. 2013b, CPL, *in press*
- Gaw, J. F., Willets, A., Green, W. H., & Handy, N. C. 1991, in Advances in Molecular Vibrations and Collision Dynamics, ed. J. M. Bowman & M. A. Ratner (Greenwich, Connecticut: JAI Press, Inc.), 170–185
- Gottlieb, C. A., Brüinken, S., McCarthy, M. C., & Thaddeus, P. 2007, JChPh, 126, 191101
- Gupta, H., Brünken, S., Tamassia, F., et al. 2007, ApJL, 655, 57
- Huang, X., Fortenberry, R. C., & Lee, T. J. 2013, ApJL, 768, 25
- Huang, X., & Lee, T. J. 2008, JChPh, 129, 044312
- . 2009, JChPh, 131, 104301
- Kendall, R. A., Dunning, T. H., & Harrison, R. J. 1992, JChPh, 96, 6796

- Kołos, R., Gronowski, M., & Botschwina, P. 2008, JChPh, 128, 154305
- Lakin, N. M., Hochlaf, M., Chambaud, G., & Rosmus, P. 2001, JChPh, 115, 3664
- Larsson, M., Geppert, W. D., & Nyman, G. 2012, Rep. Prog. Phys., 75, 066901
- Lee, T. J., & Scuseria, G. E. 1995, in Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy, ed. S. R. Langhoff (Dordrecht: Kluwer Academic Publishers), 47–108
- Martin, J. M. L., & Lee, T. J. 1996, CPL, 258, 136
- Martin, J. M. L., & Taylor, P. R. 1994, CPL, 225, 473
- McCarthy, M. C. 2013, *personal communication*
- McCarthy, M. C., Gottlieb, C. A., Gupta, H., & Thaddeus, P. 2006, ApJL, 652, 141
- McCarthy, M. C., & Thaddeus, P. 2007, JChPh, 127, 221104
- McCarthy, M. C., Travers, M. J., Kovács, A., Gottlieb, C. A., & Thaddeus, P. 1997, ApJSS, 113, 105
- Mills, I. M. 1972, in Molecular Spectroscopy - Modern Research, ed. K. N. Rao & C. W. Mathews (New York: Academic Press), 115–140
- Ohshima, Y., & Endo, Y. 1996, CPL, 256, 635
- Papousek, D., & Aliev, M. R. 1982, Molecular Vibration-Rotation Spectra (Amsterdam: Elsevier)
- Pety, J., Gratier, P., Guzmán, V., et al. 2012, A&A, 548, A68
- Raghavachari, K., Trucks, G. W., Pople, J. A., & Head-Gordon, M. 1989, CPL, 157, 479

- Sarre, P. J. 2000, MNRAS, 313, L14
- Scheiner, A. C., Scuseria, G. E., Rice, J. E., Lee, T. J., & Schaefer III, H. F. 1987, JChPh, 87, 5361
- Senent, M. L., & Hochlaf, M. 2010, ApJ, 708, 1452
- . 2013, ApJ, 768, 59
- Shavitt, I., & Bartlett, R. J. 2009, Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory (Cambridge: Cambridge University Press)
- Skurski, P., Gutowski, M., & Simons, J. 2000, IJQC, 80, 1024
- Thaddeus, P., Gottlieb, C. A., Gupta, H., et al. 2008, ApJ, 677, 1132
- Thaddeus, P., Gottlieb, C. A., Hjalmarsen, A., et al. 1985, ApJ, 294, L49
- Watson, J. K. G. 1977, in Vibrational Spectra and Structure, ed. J. R. Durrin (Amsterdam: Elsevier), 1–89
- Werner, H.-J., Knowles, P. J., Manby, F. R., et al. 2010, MOLPRO, version 2010.1, a package of ab initio programs, see <http://www.molpro.net>
- Yamamoto, S., Saito, S., Ohishi, M., et al. 1987, ApJL, 322, 55

Fig. 1.— CcCR equilibrium geometry of  $1\ ^1A'$   $l$ -C<sub>3</sub>H<sup>-</sup>.

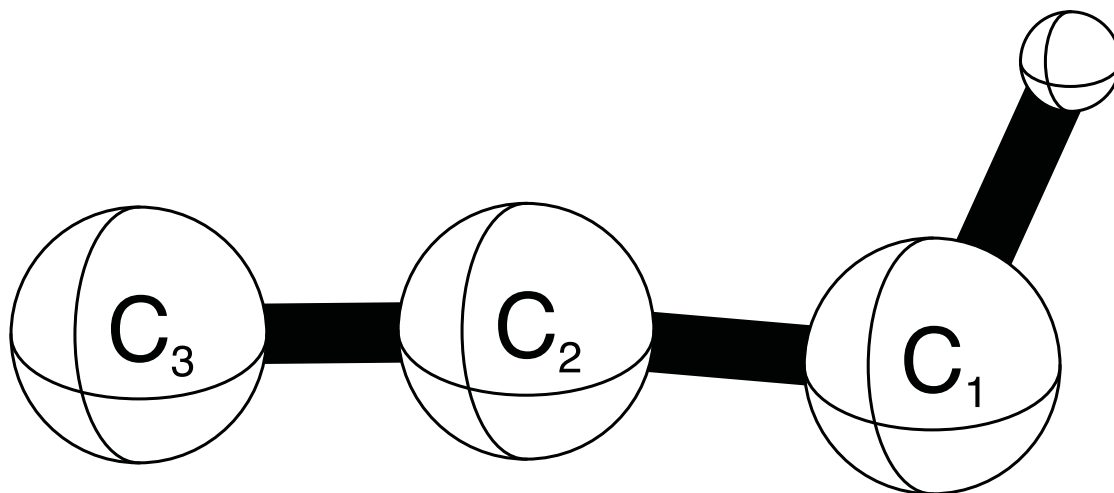




Table 1: The simple-internal CcCR QFF Quadratic, Cubic, and Quartic Force Constants (in  $\text{mdyn}/\text{\AA}^n \cdot \text{rad}^m$ )<sup>a</sup> for  $l\text{-C}_3\text{H}^-$ .

$F_{11}$	10.191 889	$F_{431}$	0.0711	$F_{1111}$	318.24	$F_{4432}$	0.24	$F_{5531}$	0.12
$F_{21}$	0.841 962	$F_{432}$	-0.4022	$F_{2111}$	0.44	$F_{4433}$	0.44	$F_{5532}$	0.22
$F_{22}$	7.312 189	$F_{433}$	-0.0735	$F_{2211}$	-1.98	$F_{4441}$	0.45	$F_{5533}$	-0.34
$F_{31}$	0.068 029	$F_{441}$	-0.5015	$F_{2221}$	5.28	$F_{4442}$	-0.34	$F_{5541}$	-0.01
$F_{32}$	-0.006 196	$F_{442}$	0.1723	$F_{2222}$	220.01	$F_{4443}$	0.56	$F_{5542}$	0.07
$F_{33}$	4.558 746	$F_{443}$	-0.0586	$F_{3111}$	0.16	$F_{4444}$	-0.81	$F_{5543}$	-0.17
$F_{41}$	-0.066 879	$F_{444}$	-0.7769	$F_{3211}$	-0.08	$F_{5111}$	0.06	$F_{5544}$	0.51
$F_{42}$	0.515 214	$F_{511}$	-0.0809	$F_{3221}$	0.80	$F_{5211}$	0.10	$F_{5551}$	0.07
$F_{43}$	0.217 498	$F_{521}$	-0.0018	$F_{3222}$	-1.41	$F_{5221}$	-0.39	$F_{5552}$	0.18
$F_{44}$	0.650 100	$F_{522}$	-0.3714	$F_{3311}$	0.72	$F_{5222}$	0.80	$F_{5553}$	0.12
$F_{51}$	0.070 974	$F_{531}$	-0.0597	$F_{3321}$	-0.80	$F_{5311}$	0.09	$F_{5554}$	-0.12
$F_{52}$	0.081 130	$F_{532}$	-0.2190	$F_{3322}$	-0.54	$F_{5321}$	0.21	$F_{5555}$	1.95
$F_{53}$	0.069 481	$F_{533}$	-0.0030	$F_{3331}$	-0.82	$F_{5322}$	0.54	$F_{6611}$	0.14
$F_{54}$	0.064 059	$F_{541}$	-0.0774	$F_{3332}$	0.46	$F_{5331}$	-0.04	$F_{6621}$	-0.49
$F_{55}$	0.404 485	$F_{542}$	0.0376	$F_{3333}$	145.05	$F_{5332}$	-0.07	$F_{6622}$	0.64
$F_{66}$	0.168 044	$F_{543}$	-0.0694	$F_{4111}$	-0.17	$F_{5333}$	-0.46	$F_{6631}$	0.03
$F_{111}$	-64.7214	$F_{544}$	-0.1425	$F_{4211}$	-0.02	$F_{5411}$	0.14	$F_{6632}$	0.06
$F_{211}$	0.5759	$F_{551}$	-0.4284	$F_{4221}$	-0.27	$F_{5421}$	0.12	$F_{6633}$	-0.14
$F_{221}$	-3.2972	$F_{552}$	-0.9210	$F_{4222}$	-0.32	$F_{5422}$	-0.49	$F_{6641}$	-0.07
$F_{222}$	-43.3783	$F_{553}$	-0.0900	$F_{4311}$	0.15	$F_{5431}$	-0.05	$F_{6642}$	-0.04
$F_{311}$	0.0659	$F_{554}$	0.0071	$F_{4321}$	-0.03	$F_{5432}$	0.31	$F_{6643}$	-0.10
$F_{321}$	-0.3042	$F_{555}$	-0.1839	$F_{4322}$	-0.46	$F_{5433}$	-0.09	$F_{6644}$	0.08
$F_{322}$	-0.0840	$F_{661}$	-0.1710	$F_{4331}$	-0.06	$F_{5441}$	0.01	$F_{6651}$	-0.04
$F_{331}$	0.1287	$F_{662}$	-0.3467	$F_{4332}$	-0.31	$F_{5442}$	0.14	$F_{6652}$	0.02
$F_{332}$	0.2601	$F_{663}$	-0.0476	$F_{4333}$	-1.42	$F_{5443}$	0.24	$F_{6653}$	-0.03
$F_{333}$	-28.7819	$F_{664}$	0.0133	$F_{4411}$	-0.63	$F_{5444}$	-0.06	$F_{6654}$	-0.10
$F_{411}$	-0.2017	$F_{665}$	-0.0708	$F_{4421}$	1.45	$F_{5511}$	0.57	$F_{6655}$	0.23
$F_{421}$	0.3282			$F_{4422}$	-1.71	$F_{5521}$	0.14	$F_{6666}$	0.86
$F_{422}$	-0.6518			$F_{4431}$	-0.17	$F_{5522}$	1.56		

<sup>a</sup>1 mdyn =  $10^{-8}$  N;  $n$  and  $m$  are exponents corresponding to the number of units from the type of modes present in the specific force constant.

Table 2: The Zero-Point ( $R_\alpha$  vibrationally-averaged) and Equilibrium Structures, Rotational Constants, CCSD(T)/aug-cc-pV5Z Dipole Moment, Vibration-Rotation Interaction Constants, and Quartic and Sextic Distortion Constants of 1  $^1A'$   $l$ -C<sub>3</sub>H<sup>-</sup> and the deuterated form with the CcCR QFF.

	C <sub>3</sub> H <sup>-</sup>	Previous <sup>a</sup>	C <sub>3</sub> D <sup>-</sup>
$r_0(\text{C}_1\text{--H})$	1.119 438 Å		1.116 446 Å
$r_0(\text{C}_1\text{--C}_2)$	1.351 595 Å		1.351 753 Å
$r_0(\text{C}_2\text{--C}_3)$	1.282 845 Å		1.282 620 Å
$\angle_0(\text{H--C}_1\text{--C}_2)$	109.491°		109.530°
$\angle_0(\text{C}_1\text{--C}_2\text{--C}_3)$	174.540°		174.643°
$A_0$	529 134.2 MHz		295 539.6 MHz
$B_0$	11 339.66 MHz		10 626.03 MHz
$C_0$	11 087.35 MHz		10 238.74 MHz
$D_J$	4.954 kHz		4.544 kHz
$D_{JK}$	0.702 MHz		0.316 MHz
$D_K$	217.543 MHz		94.897 MHz
$d_1$	-0.112 kHz		-0.253 kHz
$d_2$	-0.023 kHz		-0.052 kHz
$H_J$	3.344 mHz		16.516 mHz
$H_{JK}$	3.221 Hz		2.151 Hz
$H_{KJ}$	-3.229 kHz		-0.745 kHz
$H_K$	358.867 kHz		90.731 kHz
$H_1$	0.132 mHz		0.634 mHz
$H_2$	0.203 mHz		0.612 mHz
$H_3$	0.037 mHz		0.133 mHz
$\tau_{aaaa}$	-873.001 MHz		-380.872 MHz
$\tau_{bbbb}$	-0.021 MHz		-0.021 MHz
$\tau_{cccc}$	-0.019 MHz		-0.017 MHz
$\tau_{aabb}$	-2.766 MHz		-1.619 MHz
$\tau_{aacc}$	-0.081 MHz		0.319 MHz
$\tau_{bbcc}$	-0.020 MHz		-0.018 MHz
$\Phi_{aaa}$	355 640.661 Hz		89 988.504 Hz
$\Phi_{bbb}$	0.001 Hz		0.004 Hz
$\Phi_{ccc}$	0.000 Hz		0.001 Hz
$\Phi_{aab}$	390.158 Hz		703.204 Hz
$\Phi_{abb}$	4.265 Hz		3.112 Hz
$\Phi_{aac}$	-3 614.354 Hz		-1 445.590 Hz
$\Phi_{bbc}$	0.000 Hz		0.001 Hz
$\Phi_{acc}$	-0.271 Hz		0.151 Hz
$\Phi_{bcc}$	0.001 Hz		0.002 Hz
$\Phi_{abc}$	4.570 Hz		3.618 Hz
$\alpha^A_1$	27 922.5 MHz		11 662.9 MHz
$\alpha^A_2$	-725.5 MHz		-917.5 MHz
$\alpha^A_3$	484.8 MHz		170.2 MHz
$\alpha^A_4$	-35 092.1 MHz		-16 226.3 MHz
$\alpha^A_5$	-3 103.1 MHz		-4 597.5 MHz
$\alpha^A_6$	12 333.4 MHz		9 042.1 MHz
$\alpha^B_1$	4.2 MHz		6.9 MHz
$\alpha^B_2$	83.5 MHz		77.2 MHz
$\alpha^B_3$	45.1 MHz		40.3 MHz
$\alpha^B_4$	-12.0 MHz		-8.4 MHz
$\alpha^B_5$	-47.1 MHz		-48.4 MHz
$\alpha^B_6$	-48.6 MHz		-45.9 MHz
$\alpha^C_1$	14.8 MHz		18.3 MHz
$\alpha^C_2$	78.6 MHz		70.1 MHz
$\alpha^C_3$	38.4 MHz		39.3 MHz
$\alpha^C_4$	16.0 MHz		12.9 MHz
$\alpha^C_5$	-16.1 MHz		-15.2 MHz
$\alpha^C_6$	-78.5 MHz		-69.8 MHz
$r_e(\text{C}_1\text{--H})^b$	1.106 939 Å	1.110 Å	—
$r_e(\text{C}_1\text{--C}_2)$	1.349 832 Å	1.289 Å	—
$r_e(\text{C}_2\text{--C}_3)$	1.281 900 Å	1.363 Å	—
$\angle_e(\text{H--C}_1\text{--C}_2)$	109.529°	109.2°	—
$\angle_e(\text{C}_2\text{--C}_3\text{--C}_4)$	174.571°	171.2°	—
$A_e$	530 044.3 MHz	524.5 MHz	295 106.5 MHz
$B_e$	11 352.05 MHz	11.2 MHz	10 636.73 MHz
$C_e$	11 114.02 MHz	10.9 MHz	10 266.68 MHz
$\mu^c$	2.16 D	—	—
$\mu_x$	1.63 D	—	—
$\mu_y$	1.41 D	—	—

<sup>a</sup>CCSD(T)/aug-cc-pVQZ QFF results from Lakin et al. (2001).

<sup>b</sup>The equilibrium geometries are identical among isotopologues from the use of the Born-Oppenheimer approximation.

<sup>c</sup>The C<sub>3</sub>H<sup>-</sup> coordinates (in Å with the center-of-mass at the origin) used to generate Born-Oppenheimer dipole moment components are: H, 1.733414, -0.910473, 0.000000; C<sub>1</sub>, 1.276456, 0.098036, 0.000000; C<sub>2</sub>, -0.069613, -0.016965, 0.000000; C<sub>3</sub>, -1.352424, -0.004605, 0.000000.

Table 3: Errors in the computation of  $B_{eff}$  (in MHz) and  $D_{eff}$  (in kHz) for various small molecules.

Molecule	$B/B_{eff}$			$D/D_{eff}$		
	Experiment	Theory	% Error	Experiment	Theory	% Error
$C_3H^{-a}$	11244.9474	11213.51	0.28%	7.652	8.795	14.93%
$C_3H^{-b}$	11244.9474	11233.04	0.11%	7.652	8.366	9.34%
$HSCO^{+c}$	5636.866	5637.60	0.01%	3.1	3.116	0.53%
$HOCO^{+d}$	10691.58265	10705.44	0.13%	4.580576	4.511	1.52%
$HOCS^{+e}$	5726.66011	5730.22	0.06%	1.064	1.107	4.00%
$C_2H^{-f}$	41639.20	41781.0	0.34%	0.09697	0.0946	2.44%
$C_2H^{-f}$	41639.20	41614.0	0.06%			
$C_4H^{-g}$	4654.9449	4653.9	0.02%	0.5875	0.55	6.4%
$C_4H^{-h}$	4654.9449	4625.6546	0.63%			
$C_6H^{-i}$	1376.86298	1376.9	0.00%	0.03235	0.0270	16.5%
$C_8H^{-j}$	583.30404	583.2	0.02%	0.0042	0.0033	17%
$CN^{-k}$	56132.7562	56152	0.03%	186.427	185	0.77%
$C_3N^{-l}$	4851.62183	4850	0.03%	0.68592	0.628	8.44%
$C_5N^{-m}$	1388.860	1387.8	0.08%	0.033	0.0300	9.1%
$C_5N^{-n}$	1388.860	1386.2	0.19%			

<sup>a</sup>This work with vibrationally averaged data and the observational lines described by Pety et al. (2012).

<sup>b</sup>This work from the equilibrium rotational constants and the observational lines described by Pety et al. (2012).

<sup>c</sup>CcCR QFF data computed from vibrationally averaged  $A$ ,  $B$ , and  $C$  constants given in Fortenberry et al. (2012a) and experimental data from Ohshima & Endo (1996).

<sup>d</sup>CcCR QFF vibrationally averaged data from Fortenberry et al. (2012b) and experimental data from Bogey et al. (1988).

<sup>e</sup>CcCR QFF vibrationally averaged data from Fortenberry et al. (2012a) and experimental data from McCarthy & Thaddeus (2007).

<sup>f</sup>CcCR QFF equilibrium values (first line) and  $B_0$  (second line) from Huang & Lee (2009) and experimental data from Brünken et al. (2007a).

<sup>g</sup>CCSD(T)/cc-pVTZ  $B_e$  and  $D_e$  as well as experimental data from Gupta et al. (2007).

<sup>h</sup>RCCSD(T)/aug-cc-pVQZ  $B_e$  from Senent & Hochlaf (2010) with the experimental  $B_{eff}$  again from Gupta et al. (2007).

<sup>i</sup>CCSD(T)/cc-pVTZ  $B_e$ , CCSD(T)/cc-pVDZ  $D_e$ , and experimental data from McCarthy et al. (2006).

<sup>j</sup>CCSD(T)/cc-pVTZ  $B_e$ , SCF/DZP  $D_e$ , and experimental data from Gupta et al. (2007).

<sup>k</sup>CCSD(T)/aug-cc-pCV5Z  $B_e$ , CCSD(T)/aug-cc-pCVQZ  $D_e$ , and experimental data from Gottlieb et al. (2007).

<sup>l</sup>CCSD(T)/aug-cc-pCV5Z  $B_e$  and  $D_e$  from Kolos et al. (2008) ( $\Delta B_0$  is reported to be 0.606 MHz giving a % error of about 0.02%) and experimental data from Thaddeus et al. (2008).

<sup>m</sup>CCSD(T)/aug-cc-pCV5Z  $B_e$  and CCSD(T)/aug-cc-pVQZ  $D_e$  from Botschwina & Oswald (2008) with experimental data from Cernicharo et al. (2008).

<sup>n</sup>CCSD(T)/aug-cc-pCV5Z  $B_0$  from Botschwina & Oswald (2008) with experimental data from Cernicharo et al. (2008).

Table 4: The  $\text{C}_3\text{H}^-$  and  $\text{C}_3\text{D}^-$  CcCR QFF harmonic, VCI, and VPT2 fundamental vibrational frequencies in  $\text{cm}^{-1}$ .

Mode	Description	$\text{C}_3\text{H}^-$			Previous <sup>a</sup> $\text{C}_3\text{H}^-$		$\text{C}_3\text{D}^-$		
		Harmonic	VCI	VPT2	Harmonic	Anharm.	Harmonic	VCI	VPT2
$\nu_1(a')$	$\text{C}_1\text{--H}$ stretch	2881.9	2714.4	2713.9	2863	2723	2122.9	2036.4	2035.5
$\nu_2(a')$	$\text{C}_2\text{--C}_3$ stretch	1843.9	1804.3	1804.4	1831	1828	1832.9	1796.5	1796.5
$\nu_3(a')$	$\text{C}_1\text{--C}_2$ stretch	1117.1	1108.0	1107.9	1091	1120	1112.0	1100.9	1101.0
$\nu_4(a')$	$\text{H--C}_1\text{--C}_2$ bend	1037.8	1012.1	1011.1	1002	1022	817.0	803.8	802.7
$\nu_5(a')$	$\text{C}_1\text{--C}_2\text{--C}_3$ bend	406.7	419.4	418.9	393	368	379.1	382.4	381.9
$\nu_6(a'')$	torsion	281.0	296.8	296.1	349	297	278.9	286.7	286.1

<sup>a</sup>CCSD(T)/aug-cc-pVQZ QFF results from Lakin et al. (2001).